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(54) AMINOSILANE MODIFIED POLYURETHANE AND TREATMENT OF TEXTILE MATERIALS

(71) We, COMMONWEALTH SCIENTIFIC AND INDUSTRIAL
 RESEARCH ORGANIZATION, an Australian body corporate established under
 the Science and Industry Research Act 1949—1973, carrying on scientific and
 industrial research of Limestone Avenue, Campbell, Australian Capital Territory,
 Commonwealth of Australia, do hereby declare the invention, for which we pray
 that a patent may be granted to us and the method by which it is to be performed,
 to be particularly described in and by the following statement:—

This invention is concerned with a process for the production of polyurethane
 finishes on keratin-containing and other textile materials, which have improved
 properties.

It has been proposed heretofore to coat textiles with both polyester and
 polyether urethanes for various purposes including the shrinkresisting of wool and
 the like. However, the heretofore known coatings and finishes have not been
 entirely satisfactory because they lead to unsatisfactory handle or stiffness of the
 finished textile material.

This invention has among its objects the provision of novel processes for
 treating textile materials involving the use of amine-modified polyurethanes, and
 in particular, amino silane-modified polyurethanes, thereby to provide such
 benefits as shrinkage resistance, permanent press qualities, anti-pilling properties,
 anti-snagging, abrasion resistance, and wrinkle recovery, all with a handle
 substantially superior to that known in the prior art. The invention also provides
 methods for the preparation of the aforementioned amine-modified
 polyurethanes.

The modified polyurethane materials can be applied to textile materials to
 provide improvements to their processing and wear performance. In particular we
 have noted improvements to such properties as abrasion resistance, dimensional
 stability, pilling resistance, snagging resistance, strength, smooth drying after
 wetting or washing, and tailorability where the reduced tendency of materials to
 curl and roll on cutting, especially with knitted materials, is essentially eliminated.
 To those skilled in the art of textile fabrics improvements in these areas are
 especially advantageous.

The invention finds particular application in materials comprised wholly or
 partially of keratinous materials.

The relaxation and felting shrinkages of structures containing keratin fibres
 have been a serious problem in the textile industry. Oxidative treatments, such as
 acid chlorination, have been used widely in the past to obtain control over
 dimensional stability. Such methods, however, are objectionable because of the
 loss of tensile strength and abrasion resistance which results from the treatment.

A solution to this problem has been to coat mildly oxidised keratin fibres with
 a polymer; the combination of the two processes producing a felt free finish

without loss in tensile or abrasion properties. For most polymer systems prior chlorination is essential in that without it the polymer cannot spread on the keratin fibre.

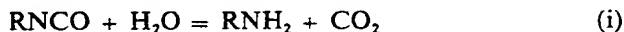
Reactive isocyanate terminated prepolymers, e.g., Synthappret LKF (Bayer), can be applied to wool without prior pretreatment to yield a fabric which is stable to laundering and drycleaning. They are of great interest in the treatment of wool materials because they can be applied from organic solvent, from water as their aqueous emulsions, or from water as solutions of their bisulphite adducts, and can be cured under mild conditions.

The principal disadvantage of such isocyanate terminated products is that the treated material is stiffened. Hence, softening aftertreatments such as dry tumbling, tumbling in the presence of steam, or tumbling with spray application of softener, washing, or drycleaning are commonly practised. Additives for incorporation into the polymer application bath e.g. Synthappret LW (Bayer) and Braxan LFB (Ciba-Geigy) are available but are not satisfactory because levels of application that produce a suitable handle invariably cause a large loss in shrinkresistance.

We have assessed the handle of treated fabrics by measurement of the flexural rigidity. Flexural rigidity is a basic factor involved in the subjective determination of handle (W. S. Howorth, J. Textile Institute, 1964, Vol. 55, T251). Flexural rigidity (as measured according to British Standard 3356:1961) is a measure of the resistance of the cloth to bending by external forces and is related to the quality of handle in the sense that cloth having a high flexural rigidity tends to feel stiff and hence has a hard handle.

In our studies on the application of isocyanate terminated products we have observed that the handle, or stiffness, of the textile material is proportional to the isocyanate content of the product in the treatment bath.

Textile materials, particularly garments, are generally treated by dipping the goods in a solution of the prepolymer in an organic solvent, for example, perchloroethylene. The excess solution is then removed and stored in a holding tank. Following drying, the garments are removed from the treatment machine, pressed if necessary, and allowed to cure in air for 4—7 days or more rapidly by exposure to steam and heat. The curing reaction is caused by water reacting with an isocyanate group to form an amine (reaction (i)) which then reacts with another isocyanate group to form a crosslink (reaction (ii)).



Textile fibres, especially wool, contain a relatively large amount of water in the form of moisture regain. During treatment of each batch water is transferred to the resin solution and partial curing occurs before the polymer is applied to the material. With successive treatments of garment batches, the isocyanate content of the resin in the storage tank decreases and the handle of the material after curing progressively improves, we believe, because the crosslink density decreases. However, if the storage tank needs replenishing or has to be discharged because of contamination with, for example, dyestuff, the handle of the treated garments becomes stiffer because of the high isocyanate content of the treatment bath. Thus the handle can be extremely variable.

The reaction of water with isocyanate groups is slow, so that although an acceptable level of handle may be obtained if the isocyanate content falls from an initial value of $\sim 5\%$ to say 2.0% , it is not industrially feasible to "age" the bath artificially by adding water. Depending on the temperature of the bath it would take some 2—10 days of ageing before the isocyanate content reached an acceptable level. An alternative would be to incorporate a catalyst for the hydroxyl group-isocyanate reaction, e.g., zinc 2-ethylhexoate ("zinc octoate"). Although the reaction time to the desired isocyanate level is greatly reduced, the difficulties are that —

(a) the reaction time is still too slow,

(b) the reaction is not stoichiometric,

(c) the polymer cures too rapidly when the garment is exposed to air.

If the polymer cures before the garment is smoothed out by pressing, unsightly and essentially permanent wrinkles can be set in.

Another way in which we have been able to increase the rate of ageing of the

bath is to incorporate compounds which contain both a free hydroxyl group and a tertiary nitrogen atom. The presence of the nitrogen group causes base catalysis of the isocyanate-hydroxyl group reaction. For example, the compounds N-ethyl diethanolamine and N,N,N',N'-tetrakis-(2-hydroxy-propyl)-ethylenediamine (Quadrol, Wyandotte Chemical Corporation), can be used to reduce the isocyanate content of the bath at an increased rate. However, the difficulties (a), (b) and (c) as above are still encountered.

We have found that certain amino functional alkoxy silanes which react rapidly and stoichiometrically (within minutes at room temperature), with isocyanate groups, offer a means of controlling the isocyanate level and thereby the handle. By lowering the average number of isocyanate groups per polymer molecule by reaction with an aminosilane, a softer handle is obtained by virtue of the reduced number of crosslinks in the final cured film. Thus, the handle can be varied at will between the maximum (as determined by the number of isocyanate groups in the polymer as received) and the minimum (as determined by the minimum number required to achieve the shrinkresist effect). We have found that substantial improvements can be obtained with those alkoxysilanes which are monofunctional with respect to amine groups or which have a number of amine groups (either primary or secondary) but which, because of steric factors, only react monofunctionally. The aminosilane must also be soluble in the polyurethane polymer or in a solvent capable of dissolving the polymer, for example, ethyl acetate, the chlorinated hydrocarbons such as perchloroethylene, or the petroleum fractions such as white spirit.

According to the present invention, there is provided a process for the production of polyurethane finishes on textile materials, wherein the polyisocyanate prepolymer of a polyol and a diisocyanate is reacted with an alkoxy silane containing a functional amino group which reacts with an isocyanate group and containing one or more alkoxy groups attached to a silicon atom, and the reacted prepolymer is applied to the material and cured thereon to an insoluble product.

Although the improvement in handle properties of the polyurethane is proportional to the amount of aminosilane reacted, a point is reached where the effectiveness of the treatment, especially for shrinkresistance, decrease rapidly. Thus, Synthappret LKF (Bayer), which has an isocyanate concentration of approximately 4.0% to 5.0% by weight, ceases to become effective as a shrinkresist agent when less than 2.0% to 2.5% isocyanate group remain after reaction.

It was also an unexpected finding that this class of amino functional alkoxy silane derivatives provided improved antiwrinkling characteristics when compared to both untreated fabric and to fabric treated with the unmodified isocyanate polymer.

Another unexpected finding was the improvement in light and thermal stability of the thin film of cured polymer on the textile material when using the alkoxy silane derivatives of poly(ether)urethanes. Poly(ether)urethanes breakdown readily under the influence of heat and light and normally require an antioxidant such as 2,2'-methylenebis (4-methyl-6-tert-butylphenol) to give adequate performance on normal wear or use of the treated textile material.

Some of the other significant advantages provided by our amino derivatives are listed below.

They provide highly effective shrinkresist treatments, even when applied in proportions smaller than the original isocyanate polymers.

In improving the handle they are effective *per se*; the conjoint application of a plasticizer or softener is not necessary, nor is a post softening treatment such as washing, tumbling spraying etc. also necessary.

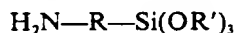
They provide flat setting, durable crease, and anti-fuzz or anti-pill formation properties. They may be used with advantage in permanent press processes in particular one developed by us; (M. A. White, Wool Technology and Sheep Breeding, Vol. 18, No. 11, Dec. 1971, p27-32).

They do not adversely affect the intrinsic properties of the fibres such as colour, tensile strength, porosity, vapour permeability and abrasion resistance so that the treated fibrous materials can be employed in any of the usual applications as in fabricating skirts, trousers, shirts and other garments. In fact, the abrasion resistance is usually improved by 10—50%.

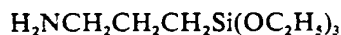
They can be used *per se* in applications from organic solvent, or in the form of aqueous emulsions, or in the form of aqueous solutions by forming the bisulphite adducts of the residual isocyanate groups.

The silane derivatives used in the invention are prepared by reacting an amino functional silane, such as γ -amino propyl triethoxy silane with 10% to 90% of the free isocyanate groups in a low molecular weight, solvent soluble, polyether (or polyester) urethane prepolymer. This simple reaction between the isocyanate groups of the polyurethane and the amino group of the silane establishes the desired silane modification of the starting polymer. The reaction is carried out at about 10°C to 150°C, preferably at about 10°C to 50°C, and more preferably at room temperature. The reaction is carried out under essentially anhydrous conditions to avoid hydrolysis of the isocyanate groups or of the alkoxy groups of the silane.

In the most preferred case the amino functional group is a primary amine and the silane is characterised by the general structure;



where R is a single bond or a divalent radical derived from an organic molecule and linking the nitrogen and silicon atoms, preferably an alkyl chain of three carbon atoms, and OR' is an alkoxy group and preferably a methoxy or ethoxy group. A particularly advantageous silane for the present invention is the proprietary product Amine A-1100 manufactured by Union Carbide. This product has the structure;



The polyether (or polyester) urethanes used as intermediates for the preparation according to the invention are widely available and used, for example, in the production of urethane foams for insulation and in the production of elastomers. Although the preparation of these intermediates forms no part of the present invention, the subject is explained in brief to illustrate the extensive range of intermediates which may be usefully employed in producing the amine derivatives of the invention.

The intermediate polyisocyanate prepolymers are provided by the reaction of (a) polyisocyanates with

(b) compounds containing at least two hydroxyl groups (such compounds will be referred to as polyols) by any of the methods described in the prior art for the reaction of isocyanates with hydroxy compounds and well known to anyone skilled in the art of organic chemistry. Such reactions should be effected in a manner such that there is a sufficient excess of (a) to ensure reaction with all the hydroxylic groups in (b) so that at the completion of the reaction there is provided a product containing free isocyanate groups.

For the purpose of the present invention it is desirable that the polyisocyanate prepolymers have a molecular weight in excess of 500, and preferably in the range 500 to 10,000 and most preferable between 1000 and 5000 and that the functionality is greater than two but most preferably between 2 and 4.

It has been found that the most suitable polyisocyanates for use in the present invention in (a) above, are those in which all the isocyanate groups are attached to aliphatic carbon atoms. Such aliphatic polyisocyanates are preferable to those containing both aliphatic and aromatic isocyanate groups and in turn these are preferable to those containing only aromatic isocyanates.

As aliphatic polyisocyanates suitable for (a) of the present invention, there may be mentioned those of structure



where k is an integer from 2 to 16 but most preferably 4 to 6, i.e., tetramethylene diisocyanate and hexamethylene diisocyanate. Other suitable aliphatic isocyanates are isophorone diisocyanate trimethylhexamethylene diisocyanate, the isomeric bis(isocyanatomethyl)-benzenes and toluenes, 1,4-bis(isocyanatomethyl)-cyclohexane and cyclohexane-1,4-diisocyanate-4,4'-methylene bis(cyclohexylisocyanate). Such aliphatic polyisocyanates may be used either alone or in a mixture with one or more of the other aliphatic polyisocyanates listed above.

As examples of aromatic isocyanates suitable for (a) of the present invention there may be mentioned 2,4-toluene diisocyanate and 2,6-toluene diisocyanate (TDI), and their commercial mixtures 4,4'-diphenylmethane diisocyanate, dianisidine diisocyanate, and the isomeric benzene, xylene and naphthalene

diisocyanates. Such aromatic polyisocyanates may be used alone or in admixture with other aromatic polyisocyanates listed above or with the aliphatic polyisocyanates listed above.

Polyols suitable for use as (b) in the present invention may have a backbone structure of the polyether, polyester, polythioether, mixed polyester polyether or mixed polyether polythio ether classes. However, due to their superior stability to hydrolysis those containing ether linkages alone are superior to those containing ester linkages.

Suitable polyols for the present invention with a polyester backbone may be prepared from the condensation of polyhydroxy compounds with polybasic acids or their anhydrides or acid halides. Such polybasic acids may be wholly or partially replaced by hydroxy acids or lactones. Phosgene may be also incorporated into such condensations producing carbonate linkages in the backbone. Examples of polybasic acids suitable for use of the present invention are succinic, adipic, pimelic, phthalic, isophthalic, terephthalic and citric acids. An example of a lactone suitable for use is caprolactone. As examples of suitable polyhydroxy compounds there may be mentioned ethylene glycol, propylene glycol, 1,4-butandiol, glycerol, 1,2,6-hexantriol, trimethylolpropane, trimethylolethane, pentaerythritol. In all such condensations it is to be understood that mixtures of all such polybasic acids or mixtures of all such polyhydroxy compounds may be used. As a particularly useful example of a polyester polyol there may be mentioned polycaprolactone and castor oil, and products from the modification of castor oil by further condensation reactions.

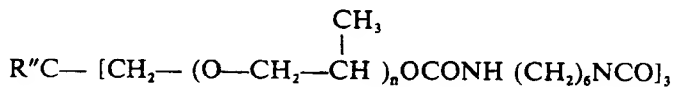
Polyols with a polyether backbone suitable for use in (b) of the present invention may be derived from the polymerisation by known methods of the following cyclic monomers containing oxygen, ethylene oxide, propylene oxide, the isomeric butylene oxides, oxacyclobutane, tetrahydrofuran and oxacyclohexane. Such monomers may be used alone or in admixture and the resultant polymerisation produce linear polyethers with a hydroxyl group at either end of the chain. Ethylene sulphide or propylene sulphide may wholly or partially replace the above oxygenated monomers resulting in products with thioether linkages in the backbone.

As particularly effective examples of such polyether compounds there may be mentioned polyethylene glycol, polypropylene glycol and polymerised tetrahydrofuran (polyoxytetramethylene) which possesses the repeating unit $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-$, most preferably in the molecular weight range 500 to 5000.

A further class of polyether polyols particularly advantageous for use as (b) in the present invention are those which can be formally considered to result from the polymerisation of the cyclic oxygen compounds such as ethylene oxide in the presence of an initiator with at least two hydroxyl groups. As examples of such initiators there are alcohols of the class $\text{HO}(\text{CH}_2)_m\text{OH}$ where m is an integer from 2 to 12 but most preferably 2 to 4, thiodiglycol, dithiodiglycol, glycerol, trimethylolethane, triethanolamine, 1,2,6-hexanetriol, pentaerythritol, sorbitol, glucose, resorcinol, phloroglucinol and the like. The use of this method leads to polyols of functionality greater than two whereas polymerisation of the cyclic oxygen compounds alone leads to difunctional compounds.

As particularly effective examples of such polyether polyols for the present invention there may be mentioned the products of condensation of glycerol or trimethylolpropane with ethylene oxide, propylene oxide or mixtures of ethylene and propylene oxide with molecular weights in the range 500—5000, but most preferably from propylene oxide with molecular weights from 1000 to 4000. A number of such products are readily available commercially as they are extensively used in the preparation of urethane foams and rubbers.

A particularly advantageous polyisocyanate prepolymer for the present invention is the proprietary product Synthappret LKF manufactured by Farbenfabriken Bayer AG., Leverkusen, Germany. This product has a structure very similar to that below



$\text{R}'' = \text{H or Et}$

$n = 14 \text{ to } 18$

As other similarly advantageous polyisocyanate prepolymers there may be mentioned Braxan LFA (Chem. Fabrik Pfersee, Augsburg, Germany) Stabifix C (Trade Mark — Henkel et Cie, Dusseldorf) Lankrothane 1304 (Lankro Chemicals, England) and Arotap M—520 (Trade Mark — Ashland Chemical Company, U.S.A.).

Polyisocyanate prepolymers which are also useful for the purposes of the present invention but are less useful than those previously mentioned are products of the Adiprene (Trade Mark) series of E. I. du Pont de Nemours and Co., U.S.A. and of the Vibrathane series of U.S. Rubber Co.

Thus, the silane modified polyurethanes have the general structure



where A is the residue of a polyether or polyester urethane with terminal isocyanate groups and having a valence of $r + p$ and greater than 2 and R and OR' are as defined previously.

It is considered within the scope of the invention to further modify the polymer by

(a) reaction of the residual isocyanate groups with a bisulphite salt so as to render the product water soluble, or

(b) reaction of the residual isocyanate groups with a blocking agent, so that the original isocyanate groups can be reformed on heating. Examples of blocking agents are phenols, thiols, alcohols, β -diketones and oximes.

Treatments as in (a) and (b) have especial advantages in that they can be utilized for delayed cure reactions in producing permanent press garments. That is the blocked derivative or the bisulphite adduct of the aminosilane modified polyurethane is applied to the fabric but not cured until the fabric has been made into the desired product. The curing then not only bonds the polymer to the fabric but also renders substantially permanent the creases or pleats which have been imparted to the fabric.

The aminosilane modified polyurethanes used in the invention may be applied to textile materials in various ways. One technique involves application in the form of aqueous emulsions. These can be prepared by the customary techniques of agitation of the modified polyurethane with water and a conventional emulsifying agent such as alkyl phenoxy poly(ethylene oxy) ethanol. The concentration of the modified polyurethane in the dispersion is not critical and may be varied on a variety of circumstances such as solubility of the modified polyurethane, the amount to be deposited on the fibres, and the viscosity of the dispersion. The dispersion may be distributed onto the textile by any of the usual methods, e.g., spraying, exhausting, brushing, dipping, padding etc. The preferred technique involves immersing the textile material in the dispersion and then passing through squeeze rolls to remove the excess liquid.

Using the bisulphite adduct of the modified polyurethane another technique involves application in the form of an aqueous solution. The solution may be distributed onto the textile by any of the usual methods as described above.

A preferred technique involves dissolving the modified polyurethane in an inert, volatile organic solvent, applying the resultant solution to the textile material, and then drying off the solvent. The most preferred technique, however, is to dissolve a known quantity of the polyurethane prepolymer in the solvent and add the desired quantity of amino silane whilst agitating the solvent. Typical of the solvents which may be used are benzene, toluene, xylene, dioxane, chlorinated hydrocarbons such as chloroform, carbon tetrachloride trichloroethylene, perchloroethylene etc., fluorohydrocarbons such as trichlorofluoromethane, 1,1,2-trichloro-1,2,2-trifluoroethane etc. In the preferred case, commercially available drycleaning solvents are used and in particular, perchloroethylene. The solution containing the modified polyurethane may be applied by any of the usual methods, for example, by spraying, padding, dipping etc. A preferred technique involves placing the textile in the cage of a drycleaning type machine and whilst the textile is tumbling in the rotating cage spraying on the solution of the modified polyurethane.

In any case, the conditions of application are so adjusted that the treated textile material contains from 0.5 to 20% solids of polymer based on the weight of the textile material. In treating textiles such as fabrics, the amount of modified

polyurethane is usually limited to a range of 0.5 to 5% to attain shrinkresistance without affecting the handle of the material.

After application of the modified polyurethane the shrinkresistance of the textile is developed by curing the polymer. Where the polymer is applied by the preferred method from solvent curing may be effected by heating, by exposure to air at ambient conditions, or, more preferably, by exposure to steam. Catalysts for the isocyanate/water reaction e.g. zinc octoate, may be included in the treatment bath if desired.

Where the polymer has been applied from aqueous dispersion or from aqueous solution (as the bisulphite adduct) adequate curing, in most cases, is effected by heating the textile in an oven at about 100°C for 5 to 30 min. If, however, the isocyanate groups remaining after preparation of the amino derivative have been blocked, slightly more severe conditions are required for unblocking and curing, for example for about 5 to 30 min at 130°C. For those conversant with the art of curing polymers it is obvious that the time required for curing will vary with such factors as the type of textile material, the reactivity of the particular polymer in question, and particularly the curing temperature so that a lower cure temperature will require a longer cure time and vice versa.

The invention is applicable to the treatment of any textile material. The textile material may be in any physical form, e.g., bulk fibres, filaments, yarns, threads, top, woven or knitted fabrics, non-woven fabrics, garments or garment parts. Fabrics, garments, and garment parts are the most suitable form for the treatment.

Any of the natural or synthetic fibres which fall in the categories below are suitable for the purpose of this aspect of the invention.

- (a) Natural fibres, as for example, flax, jute, hemp, cotton and wool and natural fibres of inorganic origin such as asbestos.
- (b) Fibres formed by the regeneration of natural materials such as casein, zein, rayon, viscose and aliginate fibres.
- (c) Man made fibres prepared from modified cellulosic materials such as cellulose acetate and triacetate.
- (d) Man made fibres of inorganic origin such as glass, metal and carbon fibres.
- (e) Fibres prepared from synthetic polymers which, for example, may fall into the following general classifications; polyamides, polyesters, polyacrylics, modified acrylics, polyvinyl chlorides, polyolefins, polyvinyl and vinylidene fibres. Blends, which are used, for example, for economic, effect or performance reasons, of any of the above classes in any ratio, are considered to be within the scope of the invention.

EXAMPLES.

All fabric concentrations of polymer refer to percent by weight of polymer solids on the weight of the fabric. Some of the Examples include control experiments employing unmodified polyisocyanate prepolymers.

Measurement of Felting Shrinkage

The decrease in area of a square 10 cm × 10 cm marked on each sample was measured after washing for 60 min in a 50 l Cubex apparatus at 40°C. Wash liquor (12.5 l) containing 0.05% soap solution and buffered to pH 6.8 was used. The total load was made up to 1 kg with knitted polyester squares. The results are the mean of those for two samples of wool. The rate of development of shrink resistance is taken as being proportional to the rate of curing.

Activity of Pre-polymer

The activity of the pre-polymer was determined by reaction of the isocyanate groups with an excess of di-n-butylamine, followed by back titration with hydrochloric acid using a few drops of a 0.1% solution of bromophenol blue in methanol as indicator. The results are expressed as '% NCO' and referred to as 'activity'. The activity is calculated from the relationship:

$$\% \text{NCO} = [4.2 \times (B - T) \times 100] / (c \times F \times V)$$

where B is the blank titre value for 50 ml 0.1—N amine using 0.1—N acid, T is the titre value for 50 ml 0.1—N amine and V ml of resin solution, c is the concentration (g/l) of the resin solution, 4.2 is one-tenth the equivalent weight of the isocyanate group, and F is the fractional solids in the polymer concentrate.

Flexural Rigidity

The handle of the treated fabrics was assessed as flexural rigidity in accordance with British Standard 3356:1961.

Fabrics

- 5 The fabrics used for the purpose of illustrating the invention are described as:
- 5 Fabric A A plain, undyed weave wool worsted fabric (10 picks/cm, 10 ends/cm, 153 g/m²) of a high felting propensity.
- 10 B An undyed single jersey knitted fabric of worsted count cover factor of 0.95 and having a high felting propensity.
- 10 C A grey commercial worsted suiting fabric of 254 g/m².

EXAMPLE 1.

- 15 Solutions of Synthappret LKF with an isocyanate content of 4.5% in perchloroethylene were modified to a range of isocyanate concentrations by addition of quantities of γ -amino-propyl-triethoxy-silane (A1100 — Union Carbide) by dropwise addition whilst stirring. The resultant modified polymers were applied to fabrics, A, B and C in such a manner that 3% by weight of the polymer was deposited. After evaporating the solvent in air and curing the polymer by exposure to steam for 30 min at 100°C the felting shrinkage was assessed on Fabrics A and B and the flexural rigidity on Fabric C.

Treatment	Area Shrinkage % Fabric A	Fabric B	Flexural Rigidity (mgm/cm)
untreated	70	51	203
Synthappret 4.5% NCO	1	1	810
3.0% NCO with A1100	1	1	650
2.0%	2	1	500
1.5%	21	4	379
1.0%	43	5	290
0.7%	60	14	235

EXAMPLE 2.

- 25 A solution of Adiprene L—100 (Du Pont, a liquid 1,4-oxybutylene glycol/TDI elastomer of approximately 2000 molecular weight and with approximately 4.0% terminal isocyanate groups) in perchloroethylene was modified to an isocyanate content of 2.9% by dropwise addition of A1100 whilst stirring. 3% by weight of the modified and unmodified polymer were applied to Fabrics A and C by padding and the polymers cured by exposure to steam for 30 min at 100°C. The following results were obtained:

	Area Shrinkage Fabric A	Flexural Rigidity Fabric C
Unmodified Polymer	2%	730
Modified Polymer	5%	420

EXAMPLE 3.

- 30 With vigorous stirring 16.8 gm of A1100 were added to 200 gm of Synthappret LKF (80% solids, 20% ethyl acetate) of 4.2% isocyanate content. Titration after reaction gave 2.15% residual isocyanate content. The polymer prepared as above

was diluted with perchloroethylene and then applied to the wool fabrics A and C (3% owf). A further sample of the modified polymer was diluted with perchloroethylene, an isocyanate/water reaction catalyst, zinc octoate, added at 1% on the weight of the polymer, and applied to fabrics A and C (3 owf). The treated samples were allowed to cure by standing in an atmosphere of 65% RH, 21°C. Samples were wash tested at varying intervals up to 7 days. The following results were obtained.

Time of Storage before Washing Testing	Catalyst in Bath	Area Shrinkage % Fabric A		Flexural Fabric C	Rigidity
		NM*	M**	NM	M
0	yes	61	45		
0	no	64	52		
1	yes	—	18		
1	no	—	45		
2	yes	12	1		
2	no	53	35		
4	yes	1	1		
4	no	39	16		
7	yes	1	1	805	483
7	no	1	2	791	497

*Not modified with A1100

**Modified with A1100

EXAMPLE 4.

The A1100 modified Synthappret of Example 3 was converted to the bisulphite adduct by the following method. Modified polymer (500 g) was stirred vigorously whilst first ethanol (500 ml) and then a solution of sodium bisulphite (62 g) in water (250 ml) were added rapidly. After 10—15 min the solution cleared and bis (3-methyl-6-*tert*-butylphenol) 4,4-sulphide Irganox (Trade Mark) 415, (5 g) was added as antioxidant. After a further 15 min water (200 ml) was added to give a translucent viscous solution containing approximately 30% solids.

The bisulphite adduct of above was diluted with water (to levels indicated below) and applied to samples of Fabric A by running wetted samples through a squeeze roll to attain a wet pick-up of 95% to 105% based on the weight of fabric. The samples were dried at 95°C for 5 min in a laboratory oven.

In a series of treatments with both the modified and unmodified products the following results were obtained:

Conc'n of Polymer Solids in Treating Solution (%)	Area Shrinkage	
	NM*	M**
3.0	1	1
2.5	7	1
2.0	25	1
1.5	48	3
1.0	68	32

*Bisulphite adduct of unmodified Synthappret LKF

**Bisulphite adduct of modified Synthappret LKF

EXAMPLE 5.

Perchloroethylene solutions of Synthappret LKF of 4.3% isocyanate content were treated with an amino functional alkoxy silane in such quantities that the final isocyanate concentration would be approximately 2.0%. This amounted, approximately, to 8—10% silane on the weight of Synthappret. The reaction was carried out in a partially enclosed vessel at room temperature and the alkoxy silane added dropwise to the Synthappret solution with vigorous stirring over 5—10 min. After that the solutions were titrated for isocyanate content and applied by padding to Fabrics A and C at 3% solids. The polymer film on the fabrics was cured by exposure to steam at 100°C for 30 min. The following results were obtained. The abbreviations UC represents Union Carbide.

Silane	Final NCO %	Area Shrinkage Fabric A	Flexural Rigidity Fabric C
Control	4.3	1	800
A1100 (UC) Amino Function $H_2N(CH_2)_3Si(OC_2H_5)_3$	2.1	1	490

EXAMPLE 6.

A 61 g/l solution of Synthappret LKF in perchloroethylene of 4.4% isocyanate content was brought to 2.5% isocyanate content by dropwise addition of 4.9 grams of A1100 per litre of solution whilst vigorously stirring.

A pair of men's worsted slacks and a jumper assembled from Fabric B were impregnated in the solution and then placed in the cage of a drycleaning machine. The garments were extracted so as to leave 95—105% by weight of liquor on the weight of garments and then the residual perchloroethylene dried off in the machine to leave approximately 3% polymer solids by weight on the garment. In a similar manner an identical pair of trousers and a knitted jumper were treated to 3% polymer solids but with unmodified Synthappret.

After drying off the solvent the garments were pressed in the customary manner. The trousers were then hung in a steam oven, heated to approximately 85°C for 30 min and then subjected to steam at atmospheric pressure for 120 min. (M.A. White, Wool Technology and Sheep Breeding, Vol. 18, No. 11, pages 27—32, 1971). The jumpers were laid flat on trays and subjected to 5 minutes steaming at 120°C in a pressure autoclave.

After treatment a panel of observers was asked to compare the handle and appearance of the treated garments. In all instances the observers could not differentiate between the appearance of the duplicate pairs. However, in all instances the observers noted that the garment treated with A1100 modified polymer was considerably softer and had a "silky" handle.

The garments were then wash tested for 1 hour in the Cubex testing apparatus and allowed to drip-dry. The following results were obtained.

Treatment composition	Crease* Sharpness	Flat* Set	Seam* Pucker
A. Trousers			
Synthappret 4.4% NCO	4—5	4—5	5.0
Synthappret 2.5% NCO A1100	4—5	4—5	5.0
B. Jumpers			
Synthappret 4.4% NCO	—	4—5	4—5
Synthappret 2.5% NCO A1100	—	4—5	4—5

*Crease Sharpness, Flat set, and Seam pucker using the AATCC Test Methods Numbers 88C:1969, 124:1969, and 88B:1969 respectively. In all cases a rating of 5.0 indicates the maximum property. Lowering ratings indicate a poorer performance.

EXAMPLE 7.

The A1100 modified Synthappret LKF of Example 3 was applied to samples of a light weight cotton sheeting from a solution in perchloroethylene to produce 3% solids on the weight of fabric. After drying off the solvent the fabric samples were pressed in the usual manner and the polymer allowed to cure in air for one week at 65% RH, 21°C.

The water soluble bisulphite adduct of the A1100 modified Synthappret LKF of Example 5 was diluted with water and 3% solids applied to samples of the cotton sheeting by padding at 100% pick-up. The samples were dried at 120°C for 3 min in a laboratory oven. In both cases the handle of the treated material was substantially softer than that treated with unmodified polymer.

The cotton sheeting samples treated with the modified polymers were assessed for water repellency using the AATCC Spray Test (Method 22—1971). Untreated fabric was rated at 0, whereas both of the fabrics treated as above rated 70—80. The ratings are based on a scale of 0 to 100; a rating of 0 meaning a complete wetting of the whole of the upper and lower surfaces of the fabric, and a rating of 100 meaning no sticking of water droplets or any wetting of the fabric surface.

EXAMPLE 8.

The treatments as described in Example 7 were carried out on samples of fabric B. Measurement of the pilling propensity were made using the Random Tumble Pill Tester (A.S.T.M. Test D1375—E). The pill count on 10 cm square samples after testing for 10 mins was 122 for an untreated sample, 49 for a sample treated with modified polymer from perchloroethylene solution, and 62 for a sample treated with the water soluble modified bisulphite adduct.

EXAMPLE 9.

The thermal stability of the water soluble bisulphite adduct of the amino siloxane modified Synthappret of Example 4 was measured in the following manner. Samples of fabric A were treated by padding to apply 0.6% bisulphite adduct and 2.4% of an aqueous emulsion of a polyacrylate, Primal K3 (Rohm and Haas), on the weight of fabric. The samples were fired for 5 min at 120°C in a laboratory dryer. The samples prepared using the A1100 modified Synthappret had a softer handle than that using the bisulphite adduct of the unmodified product.

After conditioning to 65% RH, 21°C, the treated samples were heated at 120°C for 60 min and then washed for 1 hour in a 12.5 litre Cubex. The sample treated with the bisulphite adduct prepared from the unmodified product shrunk 47% in area whereas the sample treated with the bisulphite adduct prepared from the siloxane modified product shrunk 7%. The shrinkage of samples before heating was 1%.

WHAT WE CLAIM IS:—

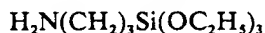
1. A process for the production of a polyurethane finish on a textile material, wherein the polyisocyanate prepolymer of a polyol and a diisocyanate is reacted with an alkoxy silane containing a functional amino group which reacts with an isocyanate group and containing one or more alkoxy groups attached to a silicon atom, and the reacted prepolymer is applied to the material and cured thereon to an insoluble product.

2. A process as claimed in Claim 1, in which the alkoxy silane has the formula



where R is a single bond or a divalent radical derived from an organic molecule and linking the nitrogen and silicon atoms, preferably an alkyl chain of three carbon atoms, and OR' is an alkoxy group.

3. A process as claimed in Claim 2, in which the alkoxy silane has the formula



4. A process as claimed in any one of Claims 1 to 3, in which the polyisocyanate prepolymer has a molecular weight of from 500 to 10,000 and a functionality greater than two.

5. A process as claimed in Claim 4, in which the prepolymer has a molecular weight of 1000 to 5000 and a functionality of 2 to 4.
6. A process as claimed in any one of Claims 1 to 5 wherein the modified prepolymer has its residual isocyanate groups blocked.
- 5 7. A process as claimed in any one of the preceding claims wherein the modified prepolymer is applied to the material as an aqueous emulsion.
8. A process as claimed in any one of Claims 1 to 6, wherein the modified prepolymer is applied to the material as an aqueous solution of the bisulphite adduct.
- 10 9. A process as claimed in any one of Claims 1 to 6, wherein the modified prepolymer is applied to the material as a solution in an organic solvent.
- 10 10. A process as claimed in Claims 7 to 9, wherein the amount of prepolymer applied to the material is 0.5 to 20% of the weight of the material.
- 15 11. A process as claimed in Claim 10, wherein the amount of the prepolymer applied is 0.5 to 5%.
- 15 12. A process as claimed in Claim 7 or Claim 8, wherein after application the material is dried and the prepolymer is cured by heating.
13. A process as claimed in Claim 9, wherein after the application the prepolymer is cured by exposure to steam.
- 20 14. A process as claimed in Claim 9, wherein after the application the prepolymer is cured by exposure to ambient conditions.
- 20 15. Textile material finished by a process according to any preceding claim.

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